7.48 g of material, bp 69.5–71.5° (5–6 mm), $n^{20}\text{D}$ 1.4994 (lit.[14] $n^{20}\text{D}$ 1.5007 for undeuterated ester), whose infrared spectrum was indicative of the title compound. Its nmr spectrum showed the ethyl group and two broad lines which upon deuterium decoupling gave two sharp resonances at 3.97 and 3.49 ppm in the ratio of 87:13, respectively. *Anal.*[15] Calcd for $BrCHDCDBrCO_2C_2H_5$: 25.00 atom % excess D. Found: 24.55%, or 1.96 deuteriums per molecule.

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(14) H. C. Murfitt and J. C. Roberts, *J. Chem. Soc.*, **146**, 371 (1944).

(15) Performed by the falling-drop method by Mr. Josef Németh, Urbana, Ill.

Structure of Electron Impact Fragments. The C_4H_4O Radical Cation from 2-Pyrone

W. H. Pirkle and Martin Dines[1]

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Abstract: Prominent in the mass spectrum of 2-pyrone is an M — CO radical cation of controversial structure. The electron impact fragmentations of the four monodeuterio-2-pyrones have been studied and the distribution of deuterium among the various daughter cations has been measured. The observed deuterium distributions allow confident exclusion of a furan-like structure for the 2-pyrone M — CO radical cation. Other structural implications of the observed isotope distributions are considered.

Owing to the difficulty in obtaining evidence pertaining to the structures of fragments resulting from electron impact induced decompositions, many workers have attempted to infer fragment structures and decomposition pathways from the precepts of ground-state solution chemistry. More recently, photochemical reactions have been used as models for gas-phase electron impact induced decompositions.[2] While the correlations thus suggested have proven to be of considerable empirical value, only rarely are those mechanistic and structural conjectures supported experimentally. Because of the importance of mass spectrometry as a tool for structural determination, the validity of these proposed structures and fragmentation schemes is of vital concern. Even so, there are few definitive studies of fragment ion structure, for the present experimental methods for investigating the structures of fragments formed within a mass spectrometer are not always applicable, and, when applicable, always yield negative evidence, thereby allowing only the exclusion of certain postulates from further consideration.

The current 2-pyrone literature is illustrative of the problems encountered in assigning structures of electron impact induced ions. Nakata, *et al.*,[3] studying the mass spectra of variously substituted 2-pyrones, noted that the principal mode of fragmentation involves initial loss of carbon monoxide[4] to produce ions which they term "electron deficient furans." Although there is no evidence that these M — CO ions are furanlike, this assignment is no less reasonable than most of the literature assignments of electron impact fragment structures. There is precedent for the recombination of the entities on either side of a carbonyl upon its expulsion as carbon monoxide,[5] and a number of satisfying canonical structures may be written for a furanlike radical cation.

In the case of 2-pyrone (**1**) Pirkle pointed out that even though the subsequent fragmentation of the C_4H_4O radical cation (the M — CO ion) produces an array of ions whose masses and abundances are apparently quite similar to those produced upon the fragmentation of the furan molecular ion, the assumption that the two isomeric C_4H_4O radical cations are both furanlike would be in error.[6] Experimentally, Pirkle found that the *m*/*e* 39 peak arising from loss of a formyl radical (or from consecutive loss of carbon monoxide and a hydrogen atom) from the C_4H_4O radical cation was shifted to *m*/*e* 40 in the case of 2-pyrone-3-*d* but remained principally at *m*/*e* 39 in the spectrum of 2-pyrone-6-*d*. Observing that the symmetry of a furanlike C_4H_4O radical cation would necessitate the equivalence of hydrogens 3 and 6 (eq 1) Pirkle concluded that the C_4H_4O radical cation from 2-pyrone cannot have cyclic furanlike structure **2** since the M — CO ions derived from 2-pyrone-3-*d* and 2-pyrone-6-*d* do not fragment identically. Noting that reasoning of the type commonly used in assigning structures to electron

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(1) Archer Daniels Midland Fellow, 1966–1967; Union Carbide Fellow, 1967–1968.

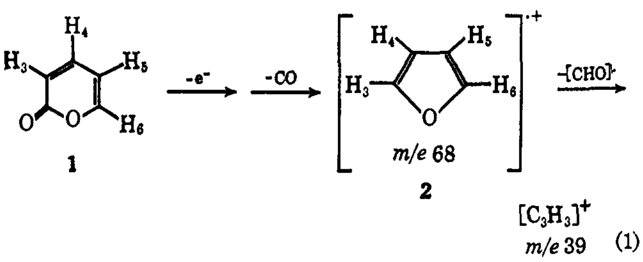
(2) For examples, see M. M. Bursey and L. R. Dusold, *Tetrahedron Letters*, 2649 (1967); S. Meyerson, I. Puskas, and E. K. Fields, *J. Am. Chem. Soc.*, **88**, 4974 (1966); N. J. Turro, D. S. Weiss, W. F. Haddon, and F. W. McLafferty, *ibid.*, **89**, 3370 (1967).

(3) H. Nakata, Y. Hirata, and A. Tatematsu, *Tetrahedron Letters*, 123 (1965).

(4) Although it is unnecessary to consider the source of the expelled carbon monoxide to interpret the isotope distributions to be presented, it should be pointed out that there is considerable analogy for carbonyl groups being expelled as carbon monoxide. For examples, see J. H. Beynon, G. K. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959); J. P. McCollum and S. Meyerson. *J. Am. Chem. Soc.*, **85**, 1739 (1963); J. M. Wilson, M. Ohashi, H. Budzikiewicz, C. Djerassi, S. Ito, and T. Nozoe, *Tetrahedron*, **19**, 2247 (1963); P. Beak, T. H. Kinstle, and G. A. Carls, *J. Am. Chem. Soc.*, **86**, 3833 (1964). Of even greater relevance, it has been shown by ^{13}C labeling that a substituted 2-pyrone loses its carbonyl carbon with the initial carbon monoxide expulsion [R. A. W. Johnstone, B. J. Millard, F. M. Dean, and A. W. Hill, *J. Chem. Soc.*, 1712 (1966)].

(5) See J. H. Beynon, "Mass Spectroscopy and Its Application to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p 259.

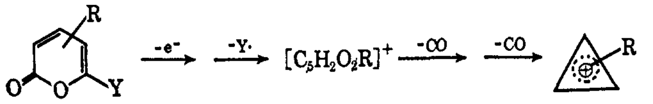
(6) W. H. Pirkle, *J. Am. Chem. Soc.*, **87**, 3022 (1965).



(1)

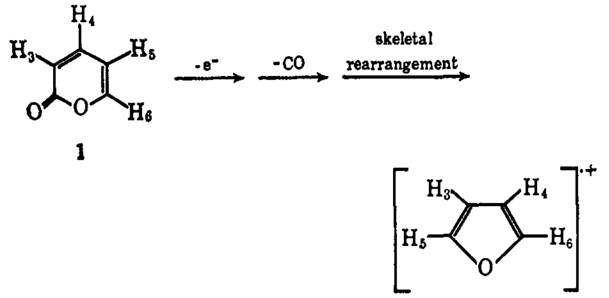
impact fragments would have, in the case of 2-pyrone, led to an erroneous conclusion, Pirkle cautioned against undue reliance on electron impact fragment structures inferred from indirect circumstantial evidence.

Brown and Green[7] point out that Pirkle's isotopic distributions can be explained by invoking an alternative fragmentation pathway. Examples are cited in which substituted 2-pyrones initially lose the 6 substituent and subsequently fragment to yield substituted cyclopropenium ions[3] (eq 2). Brown and Green note



(2)

that Pirkle's data suggest this pathway is to some extent operative and claim that the existence of this alternate source of C_3H_3 cations would invalidate the conclusion that the C_4H_4O radical cation cannot have the furanlike structure **2**. Obliged to explain why 2-pyrone-3-*d*-derived furanlike C_4H_3DO radical cations would fragment almost exclusively to C_3H_2D cations, Brown and Green suggest the alternate possibility that C-3 (or C-4) of a furanlike C_4H_4O radical cation might arise from C-3 of 2-pyrone.[8] As a consequence of such a rearrangement (eq 3), the hydrogens on C-5 and C-6 would become equivalent as well as those on C-3 and C-4. In the view of Brown and Green[7] and of Budzikiewicz, Djerassi, and Williams,[9] the question of the structure of the C_4H_4O radical cation was reopened.



(3)

A portion of the argument presented by Brown and Green suffers from internal inconsistency. To successfully challenge Pirkle's contention that the majority of the 2-pyrone M − CO radical cations are not furanlike, Brown and Green must be able to explain his labeling data in terms of a furanlike ion. The view that the major portion of the 2-pyrone C_4H_4O radical cations may be furanlike and that the reported deuterium distributions may be explained by the operation of the M − 1 sequence is contradictory to Brown and Green's expressed view that "the similarity of the mass spectra of furan (I) and 2-pyrone (II) below *m/e* 68 and especially the correspondence of the metastable peak shapes (determined in this laboratory on an Atlas CH-4 mass spectrometer) leaves little doubt that the major ions of mass 68 in the spectra of I and II are identical. . ."[7] Brown and Green must argue that C_3H_3 ions formed *via* the M − 1 sequence could, when superimposed upon the fragmentation of furanlike C_4H_4O ions, give rise to the deuterium distributions observed in the spectra of the labeled 2-pyrones. Inspection of the original distribution data makes it clear that the M − 1 sequence would have to contribute heavily (approximately 50 ± 10%) to the C_3H_3 ion abundance in order to explain the distribution data in terms of a principal furanlike ion.[10] Since this source of C_3H_3 cations is not available in the case of furan, it would be expected (provided furan and 2-pyrone each lead to the same major C_4H_4O radical cation) that the ratio of the abundance of C_3H_3 cations to C_4H_4O radical cations would be approximately 50% greater for 2-pyrone than for furan. From data in either Pirkle's original paper or in Table I, it may be seen that the ratio of the abundance of C_3H_3 cations (*m/e* 39) to C_4H_4O radical cations (*m/e* 68) is 1.18 for furan and 1.15 for 2-pyrone. The near identity of these ratios precludes the M − 1 pathway as an important source of C_3H_3 cations *unless the two major C_4H_4O radical cations fragment in rather dissimilar fashions.* The argument of Brown and Green *is* tenable *if* they abandon their claim that the major C_4H_4O ions from furan and from 2-pyrone are identical.

The suggestion by Brown and Green that Pirkle's isotope distributions might be explained by a rearrangement in which H_3 and H_4 of 2-pyrone become equivalent can be tested experimentally through examination of the mass spectra of the appropriately deuterated 2-pyrones.

Other workers are concerned with the structure of the 2-pyrone-derived C_4H_4O radical cation. Pike and McLafferty[11] have observed appreciable differences in the relative abundances of the metastable ions arising from the decomposition of the C_4H_4O molecular ions of furan and from the C_4H_4O M − CO ions from 2-pyrone. This is considered to demonstrate that the isomeric ions are not identical in both structure and energy. McLafferty's method does not allow a structural assignment to be made for either ion, however. Bursey and Dusold,[12] addressing themselves to the effect of substituents on the amount of energy released upon decarbonylation of the molecular radical cations of substituted 2-pyrones, conclude that their data are consistent with nonfuranlike structures for the respective M − CO radical cations. In the case of some sub-

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(7) P. Brown and M. M. Green, *J. Org. Chem.*, 32, 1681 (1967).

(8) The assumption that there is no concomitant hydrogen migration seems implicit in this suggestion.

(9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 208.

(10) This value represents that fraction which must be subtracted from the *m/e* 39 abundance in the case of 2-pyrone-6-*d* and from the *m/e* 40 abundance in the case of 2-pyrone-3-*d* so that the remaining *m/e* 39 and 40 abundances are reasonably similar for these two isomers. While no really good correspondence can thus be obtained for the original data, a value of 55% seems a reasonable compromise. For the newer data in Table I, a calculation of this sort leads to the estimate that the M − 1 sequence must contribute 47% of the *m/e* 39 ions (for 2-pyrone-6-*d*) and *m/e* 40 ions (for 2-pyrone-3-*d*) if the remaining *m/e* 39 and 40 abundances are to correspond for the two isomeric labeled pyrones.

(11) W. T. Pike and F. W. McLafferty, *J. Am. Chem. Soc.*, 89, 5954 (1967).

(12) M. M. Bursey and L. R. Dusold, *Chem. Commun.*, 712 (1967).

Table I. Ion Abundances Above m/e 30[a]

m/e	Furan	2-Pyrone[b]	2-Pyrone-3-d	2-Pyrone-4-d	2-Pyrone-5-d	2-Pyrone-6-d	6-Chloro-2-pyrone
132							8.4
130							27
98						6.3	
97		5.1	76	68	77	84	
96		74	17	18	19		6.0
95		18				14	100
70			5.0	6.7	6.1	4.4	
69			94	83	95	100	
68	85	87					
51		2.5	6.2	5.5	5.0	5.2	
50		5.6	4.8	5.0	4.9	4.5	
43			11 (10)[c]	3.9	10 (10)[c]	13	
42	7.4	17	9.3 (12)[c]	21	15 (16)[c]	3.0	
41			35	38	38	33	7.2
40	13	33	100	100	100	48	5.5
39	100	100	34	32	30	77	74
38	14	23	16	16	14	19	20
37	8.3	14	10	11	9.2	14	14

[a] Generally, only those values of at least 5% of the base peak are reported. [b] The values for 2-pyrone represent the average of three runs on different samples. [c] Values from an alternate run on a different sample.

stituted 2-pyrones, Johnstone, *et al.*, have expressed a preference for M − CO radical-cation structures other than ionized furan systems, although the basis for this preference seems highly speculatory.[13]

Nakata and Tatematsu, in a recent paper concerned with the structure of 2-pyrone M − CO ions, have claimed that fragmentation of a substituted 2-pyrone occurs at least partly through an intermediate in which bonding has occurred between C_3 and O_1.[14] This claim is based upon the observation of metastable peaks in the mass spectrum of 3-bromo-4,6-dimethyl-2-pyrone which support the transitions shown below. These workers *assume* that the second carbon monoxide expelled has incorporated both C_3 and O_1 and hence argue that there is bonding between C_3 and O_1 prior to the second decarbonylation. Implicit in this argument is the assumption that there have been no prior rearrangements which cause atoms other than C_3 and O_1 to be incorporated into the second carbon monoxide. Such rearrangements can be envisioned. Since there is no evidence that C_3 and O_1 are really incorporated into the second expelled carbon monoxide, there is no evidence of prior C_3–O_1 bonding. Hence, the statement "the. . .result clearly shows that an intermediate having the C_3–O_1 bond is involved. . ." is incautious and possibly in error. Moreover, whatever may be the structure of the C_6H_7O cation (the precursor of the second expelled carbon monoxide), it has no bearing upon the structure of the M − CO ion which is, in fact, the C_6H_7BrO radical cation.

$$[C_7H_7BrO_2]\cdot^+ \xrightarrow{-CO} [C_6H_7BrO]\cdot^+ \xrightarrow{-Br\cdot} [C_6H_7O]^+ \xrightarrow{-CO} [C_5H_7]^+$$

The experiments whose results are the least ambiguous and potentially the most useful in inferring possible structures of the 2-pyrone M − CO ion are determinations of how isotopic labels, specifically placed in 2-pyrone, are distributed among the fragments arising from the M − CO ion. Toward this end, the four monodeuterio-2-pyrones were synthesized and their electron impact induced fragmentations studied.

Results and Discussion

Relative ion abundances in the mass spectra (70 eV) of the compounds to be subsequently discussed appear in Table I. In the case of the deuteriated 2-pyrones, these values have been corrected for small amounts of unlabeled 2-pyrone present.

The 2-pyrone molecular ion decomposes by two principal pathways, either decarbonylating to a radical cation (*m/e* 68) or losing a hydrogen atom to give an M − 1 fragment (*m/e* 95). Both of these ions ultimately yield C_3H_3 cations. The *m/e* 68 ion further fragments *via* two alternate sequences, losing either neutral C_2H_2 (metastable observed at *m/e* 25.9) to produce a C_2H_2O radical cation (*m/e* 42) or losing the equivalent of a formyl radical to produce a C_3H_3 cation.[15] The latter process may involve either direct loss of a formyl radical or stepwise loss of carbon monoxide and a hydrogen atom. The presence of a metastable peak appropriate to loss of the formyl radical is somewhat uncertain, but well-defined metastable peaks (*m/e* 23.6 and 38.0) are observed for the sequential loss of carbon monoxide and hydrogen.

The observation of a broad flat-topped metastable peak at *m/e* 16.0 attests to the fact that the M − 1 ion from 2-pyrone loses two molecules of carbon monoxide simultaneously[16] to yield a C_3H_3 cation. Less intense metastables at *m/e* 47.3 and 22.7 indicate this double decarbonylation also occurs in a slower stepwise fashion. These interconnected processes are shown in Scheme I.

It cannot be determined from the spectrum of 2-pyrone what fraction of the total C_3H_3 cations produced arises *via* the double decarbonylation of the M − 1 ion and what fraction arises from the C_4H_4O radical cation. The answer to this question is of course relevant to one of Brown and Green's rationalizations of

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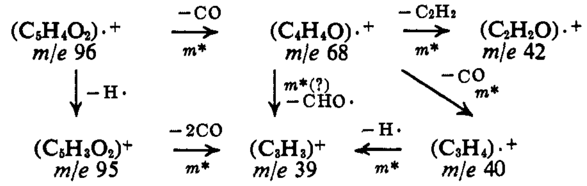
(13) R. A. W. Johnstone, B. J. Millard, F. M. Dean, and A. W. Hill, *J. Chem. Soc.*, 1712 (1966).

(14) H. Nakata and A. Tatematsu, *Tetrahedron Letters*, 4101 (1967).

(15) Dr. P. Brown, in a private communication, has pointed out the possibility that the C_4H_4O radical cations affording C_3H_3 cations may not be the same (in energy, structure, or both) as the C_4H_4O radical cations giving C_2H_2O radical cations and C_2H_2. This possibility cannot be excluded and should be borne in mind during the subsequent discussions.

(16) More rigorously, one can only say that both molecules of carbon monoxide are lost after the M − 1 ion has been accelerated but prior to its being focused. Rapid stepwise double decarbonylation is not to be excluded. This point has previously been overlooked.[8,13]

Scheme I. Partial Fragmentation Scheme for 2-Pyrone



Pirkle's data. The following discussion of the electron impact induced fragmentation of 6-chloro-2-pyrone has some bearing on the question of the importance of the M − 1 pathway in 2-pyrone.

The major fragmentation pathway for 6-chloro-2-pyrone (see Table I) involves loss of chlorine to yield a $C_5H_3O_2$ cation which undergoes double decarbonylation to a C_3H_3 cation just as does the $C_5H_3O_2$ M − 1 cation from 2-pyrone. If it could be established that the differently derived $C_5H_3O_2$ cations fragment identically, then, in the case of 2-pyrone, an estimate could be made of the fraction of C_3H_3 cations arising *via* the M −1 cation. It is clear that the $C_5H_3O_2$ cation from 6-chloro-2-pyrone must arise from loss of the 6 substituent (chlorine). That the isomeric ion derived from 2-pyrone must also arise from loss of the 6 substituent (hydrogen) follows from the observation that, for 2-pyrone labeled with deuterium in either the 3, 4, or 5 position, appreciable quantities of M − 1 ions (17–19%) but virtually no M − 2 ions (1.0 ± 0.5%) are produced. However, in the case of 2-pyrone-6-*d*, M − 2 ions (14.3%) but not M − 1 ions (1.8 ± 0.4%) are observed. The demonstration that both $C_5H_3O_2$ cations arise from loss of the 6 substituent from a 2-pyrone is consistent with, but not sufficient proof of, a common structure. Further evidence pertaining to the possible equivalency of these two cations is derived from a comparison of the intensity ratios of the metastable peaks (at *m/e* 16.0 and 47.3) produced by subsequent fragmentation of each of these ions. If the two ions are identical, these ratios should be identical.[17] For the 6-chloro-2-pyrone-derived $C_5H_3O_2$ cation, the ratio of the heights of the metastable peaks at *m/e* 16.0 and 47.3 is 28 ± 1. The corresponding value for the 2-pyrone-derived cation is 28 ± 3.[18] The similarity of these two metastable abundance ratios is also consistent with, but not proof of, the hypothesis that the two $C_5H_3O_2$ cations are of a common structure and similar energy. By *assuming* that the isomeric C_5H_3O ions fragment identically (*i.e.*, that the ions are identical), abundances of the *m/e* 95 and 39 ions from the fragmentation of 6-chloro-2-pyrone can be used to determine the fraction of the C_3H_3 cations in the spectrum of 2-pyrone which is produced by fragmentation of the M − 1 $C_5H_3O_2$ cations. From the assumption, it follows that approximately 13% (0.74 × 18%) of the C_3H_3 cations in the 2-pyrone spectrum arise *via* the M − 1 sequence. Approximately 47% of the C_3H_3 cations must arise *via* the M − 1 sequence if its operation is to account for the dissimilar deuterium distributions observed in the C_3H_3 (or C_3H_2D) cations from 2-pyrone-3-*d* and from 2-pyrone-6-*d* (see Table I).

Table II. Ion Abundances after Correction for the M − 6-Substituent Pathway[a]

m/e	Furan	2-Pyrone	2-Pyrone-3-*d*	2-Pyrone-4-*d*	2-Pyrone-5-*d*	2-Pyrone-6-*d*
98						6.3
97		5.7	80	78	80	83
96		84				
70			5.3	7.8	6.4	4.4
69			100	97	100	100
68	85	100				
51		2.8	6.6	6.4	5.4	5.2
50		6.4	5.1	5.8	5.3	4.5
43			12	4.3	11	13
42	7.4	20	8.5	23	15	3.0
41			36	43	39	32
40	13	37	93	100	88	47
39	100	100	32	33	27	66
38	14	23	15	16	13	16
37	8.3	14	11	13	10	12

[a] With minor exceptions, abundances greater than 5% of the base peak are indicated.

Table II shows the isotopic distributions among the cationic fragments from each of the singly deuterated 2-pyrones after compensation for the M − 1 (or, in the case of 2-pyrone-6-*d*, the M − 2) fragmentation pathway.[19] It must be reiterated that the values in Table II are obtained with the aid of a correction based upon the *assumed* identity of the fragmentation pathways of the isomeric $C_5H_3O_2$ cations derived from 6-chloro-2-pyrone and 2-pyrone and that the evidence for the identity of the fragmentation pathways is circumstantial. Accordingly, the assumption based on this evidence may be in error. However, the conclusions drawn from the data in Table II are consistent with those to be subsequently derived in an independent manner.

It is clear from Table II that deuterium in either the 3, 4, or 5 position of 2-pyrone is preferentially incorporated into the (formerly) C_3H_3 cation while deuterium in the 6 position is preferentially excluded from this cation. Neither of the arguments of Brown and Green suffice to account for these isotope distributions. The M − 1 pathway would appear to be too minor a contributor of C_3H_3 cations to alter Pirkle's original conclusion that the M − CO ion is nonfuranlike, while the dissimilar fates of the 5 and 6 deuteriums preclude any rearrangements which produce equivalency of the 3 and 4 positions and of the 5 and 6 positions.

From data in Table II it may be seen that the ratio of the abundances of *m/e* 39 ions to *m/e* 68 ions for furan is rather different than for 2-pyrone *after compensation for the M − 1 pathway of the latter.* These dissimilar ratios (1.18 *vs.* 1.0) are consistant with the claim of Pike and McLafferty that the furan C_4H_4O radical cation is not identical with the 2-pyrone C_4H_4O radical cation.[11]

Consideration of an additional fragmentation pathway of the C_4H_4O radical cation provides compelling

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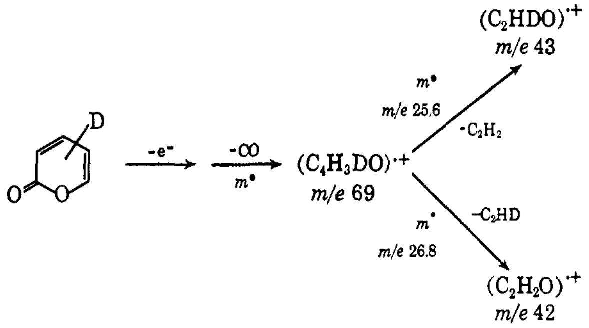
(17) This method of testing for possible identity of isomeric electron impact product ions has recently been advocated by F. W. McLafferty and T. W. Shannon, *J. Am. Chem. Soc.*, **88**, 5021 (1966).

(18) The greater uncertainty in the latter value arises as a consequence of the uncertainty involved in compensating for partial overlap of the metastable peak at mass 47.3 by a more intense metastable peak at *m/e* 48.2 arising from decarbonylation of the 2-pyrone molecular ion.

(19) Corrections for the M − 1 pathway were made by ascertaining, as far as possible, how the *m/e* 95 ion in the spectrum of 6-chloro-2-pyrone fragments, *assuming* that all the labeled 2-pyrone M − 1 (or M − 2 in the case of 2-pyrone-6-*d*) ions fragment similarly, and subtracting the contributions of the M − 1 ion and its fragments from the spectra of the labeled pyrones. Due allowance must be made for the fact that the M − 1 ions of three of the four labeled pyrones have *m/e* values of 96 and give *m/e* 40 ions upon double decarbonylation. The only significant corrections involved are in the case of the (nominal) C_3H_3 cations. Other corrections (particularly those of *m/e* <39) are somewhat uncertain, uniformly small, and of little present significance.

evidence that this ion is not furanlike. The C_4H_4O radical cation can lose a neutral C_2H_2 species to produce a C_2H_2O radical cation (*m/e* 42). The metastable peak for this transition is observed at *m/e* 25.9. When derived from one of the deuterated 2-pyrones, the labeled M − CO radical cation, C_4H_3DO, may lose either C_2HD or C_2H_2, these losses resulting in the observation of metastable peaks at either *m/e* 25.6 or 26.8. When both these metastables are observed, they reflect the relative amounts of C_2HD and C_2H_2 eliminated from the C_4H_3DO radical cations. Scheme II illustrates this situation. These ratios are observed to be 1.3 ± 0.1, >5, 1.2 ± 0.1, and ~0 for the 2-pyrones deuterated respectively at the 3, 4, 5, or 6 positions. By considering the relative abundances of the C_2HDO (*m/e* 43) and C_2H_2O (*m/e* 42) radical cations in the spectra of each of these labeled pyrones, corresponding ratios of 0.85, 5.4, 1.5, and 0.23 are obtained. While these two sets of ratios are quite similar, they need not be identical since the latter set of values, obtained through consideration of the total abundances of ions at *m/e* 42 and 43, will be sensitive to contributions of ions from other sources. Since the two sets of ratios do correspond closely and since ratio values obtained from duplicate runs and with different samples show little variation from those just cited, it is believed that these ratios accurately reflect the actual deuterium distributions.

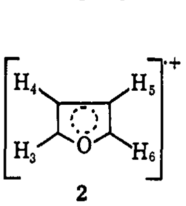
Scheme II. Partial Fragmentation Scheme for Deuterio-2-pyrones



Consideration of the ratios of C_2HD loss to C_2H_2 loss for the deuterated pyrones makes it clear that deuterium in either the 3 or the 5 position is about equally distributed between the (nominally) C_2H_2 fragment and the C_2H_2O radical cation,[20] while deuterium in the 4 position is almost always lost to the C_2H_2 species. Deuterium in the 6 position is preferentially retained by the C_2H_2O radical cation.

Summary and Conclusion

The deuterium distributions observed among the (nominally) C_3H_3 ions originating from the deuterated M − CO ions indicate that deuterium in the 6 position of 2-pyrone has not become equivalent in the M − CO ion to that originally in either the 3, 4, or 5 position. This fragmentation sequence does not give information regarding the possible equivalency (in this ion) of deuterium originally in the 3, 4, or 5 position. *Assuming* that the method by which the spectra of the labeled pyrones have been corrected for the M − 1 sequence is valid, it is clear that those C_4H_4O radical cations which formally lose formyl radicals cannot be of the symmetry of the furanlike **2** or the tricyclic **3**. The uniqueness of the 6 deuterium is consistent with the M − CO ion having a structure such as the cyclobutenyl ion **4**, the bicyclobutane ion **5**, the open-chained ion **6**, the cyclopropenyl ion **7**, or several other possibilities.



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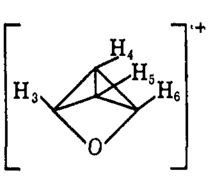

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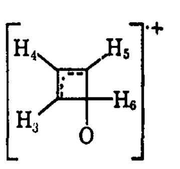

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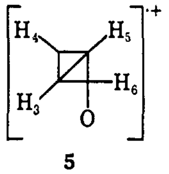

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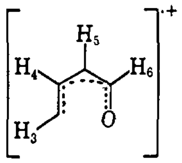

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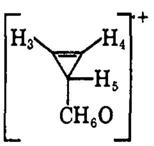

7

From consideration of the deuterium distributions observed when the deuterated C_4H_4O radical cation loses (nominally) C_2H_2, it is apparent that the 3 and 5 positions of 2-pyrone have become equivalent at or prior to the C_4H_4O radical cation stage while the 4 and 6 positions remain unique. These deuterium distributions may be accounted for by either of two alternatives. (a) If the 2-pyrone protons retain their uniqueness in the molecular ion, then the observed deuterium distributions would require that the M − CO ion have unique 4 and 6 positions but equivalent 3 and 5 positions. In this event, the M − CO ion might either be cyclobutenyl ion **4** or bicyclobutane ion **5**. The furanlike **2**, the tricyclic ion **3**, the open-chain ion **6**, and the cyclopropenyl ion **7** do not, in this alternative, fulfill the symmetry requirements imposed by the observed deuterium distributions. (b) If the 2-pyrone molecular ion has a structure such that the 3 and 5 protons have become equivalent while the 4 and 6 protons are still unique, then simple C_4H_4O structures having the requisite symmetry to describe the M − CO ion might be the cyclobutenyl ion **4**, the bicyclobutanelike ion **5**, the open-chain ion **6**, or the cyclopropenyllike ion **7**. The furanlike structure **2** and the tricyclic structure **3** are excluded by the final uniqueness of the 4 and 6 deuteriums as are all M − CO ion structures having two sets of two equivalent hydrogens or sets of three or four equivalent hydrogens.

The present study does not allow a choice to be made between alternatives a or b nor does it give any reason to prefer one allowed structure over another. It should be made clear that not all possible symmetry-allowed structures for the 2-pyrone M − CO ion have been explicitly indicated;[21] only a representative selection has been mentioned.

The deuterium distributions observed for the two M − CO ion fragmentation schemes (*i.e.*, formal loss of a formyl radical or loss of neutral C_2H_2) are consistent with, but do not require, both schemes originating from

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(20) It is felt that nonidentical values for these ratios (*i.e.*, 1.3 ± 0.1 *vs.* 1.2 ± 0.1 and 0.85 *vs.* 1.5) reflect experimental error rather than a real inequality of positions 3 and 5 in the C_4H_4O radical cation. One must also bear in mind that discussions of ion structure must necessarily refer to the structure of predominant ions and that not all ions of a given composition need have the same structure. Hence, the presence of minor amounts of isomeric ions might partially mask the equivalency of the 3 and 5 positions in the C_4H_3DO radical cation.

(21) For example, in **4**, **5**, **6**, and **7**, the hydrogen on C-6 may equally well be on oxygen so far as the ion symmetries go.

a common C_4H_4O radical cation. Should there be two M − CO ions, it is clear that neither can be the furanlike **2** or the tricyclic **3**. Accordingly, it is possible to dismiss the *a priori* "reasonable" furanlike structure from further consideration.

Experimental Section

General. Unless otherwise specified, the chemicals used were of reagent grade and were not further purified. All electron impact spectra were determined on an Atlas CH-4 instrument by Mr. J. Wrona, with the exception of those from which were measured the relative heights of the metastables arising from loss of one and two molecules of carbon monoxide from 2-pyrone and 6-chloro-2-pyrone. These spectra were determined by Dr. W. Pike of Purdue University on a Hitachi RMU-6A. Normally, the spectra were run at an ionizing voltage of 70 eV. However, low ionizing voltages (~10 eV) were used to obtain the spectra of the deuteriated 2-pyrones from which the extents of deuterium labeling were ascertained. The 70-eV spectra were then corrected by the usual method for the presence of minor amounts of unlabeled 2-pyrone. In each instance nmr spectroscopy verifies the assigned position of deuteration.

2-Pyrone. Good yields of 2-pyrone were achieved using the method of Zimmerman.[22]

6-Chloro-2-pyrone. The following method represents an improvement on the reported preparation.[23] Into a 50-ml distilling flask was added 9.96 g (0.0765 mole) of glutaconic acid (Aldrich Chemicals), the flask was cooled in an ice bath, and 30.0 g of phosphorus pentachloride was added portionwise (exothermic reaction). The flask was heated on a steam bath for 5 min and fitted with a short Vigreaux column, distilling head, and condenser, and the product was distilled at 67° (0.9 torr). The clear distillate (7.72 g, 0.0595 mole) crystallized on standing and melts at 27° with no further purification (lit.[21] mp 27°). The sample for which the mass spectrum was determined was previously sublimed at 10^{-2} torr.

2-Pyrone-6-*d*. To a solution of 2.783 g of 6-chloro-2-pyrone in 15 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride) was added 5.8 g of sodium iodide which had been vacuum dried (95°, 0.7 torr) for 2 hr. The mixture was allowed to stand for 4 hr at room temperature and was then added to a mixture of deuterioacetic acid (10 ml) and vacuum-dried zinc dust (15 g). After 12 hr at 25°, the resulting red solution was diluted with 100 ml of methylene chloride and the zinc removed by filtration. The zinc was washed with methylene chloride, and the combined filtrates were washed first with water, then with 10% sodium carbonate solution, and finally dried over anhydrous sodium sulfate. Evaporation of the solvent left 0.985 g of oil which was first purified by chromatography on silica gel and then distilled to yield 0.814 g of 2-pyrone-6-*d* of 96% isotopic purity.

2-Pyrone-4-*d*. This material was prepared from glutaconic-3-*d* acid by a procedure similar to that used for 2-pyrone-6-*d*. The glutaconic-3-*d* acid was obtained by the sodium borodeuteride reduction of ethyl acetonedicarboxylate and the subsequent hydrolysis and dehydration of the reaction product. The 2-pyrone-4-*d* ultimately obtained was of 94% isotopic purity.

2-Pyrone-5-*d*. Dried zinc dust (40.0 g) was added to a solution of 4.024 g of 5-bromo-2-pyrone[24] in 35 ml of deuterioacetic acid and the mixture blanketed with dry nitrogen. After 24 hr at room temperature and then 48 hr at 80°, the slurry was diluted with water (75 ml), the zinc pulverized, and the mixture filtered. The zinc was washed twice with 50-ml portions of hot water, and the filtrates were combined. The zinc was then washed with three 75-ml portions of methylene chloride, these portions being then used for the extraction of the aqueous filtrate. The combined methylene chloride extracts were twice washed with dilute sodium bicarbonate and dried over anhydrous sodium sulfate, and the solvent was evaporated to leave 0.927 g of a tan oil. Continuous ethereal extraction of the aqueous raffinate for 3 days yielded less than 25 mg of additional oil. Distillation at 0.5 torr gave 0.674 g of 2-pyrone-5-*d* of 87–88% isotopic purity.

2-Pyrone-3-*d*. In a manner exactly parallel to that described for 2-pyrone-5-*d*, 2-pyrone-3-*d* (0.628 g) was prepared by the reduction of 3-bromo-2-pyrone[24] (2.60 g) and was of 93% isotopic purity.

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[22] H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

[23] N. Bland and J. F. Thorpe, *J. Chem. Soc.*, **101**, 857 (1912).

[24] The preparation of 5-bromo-2-pyrone and 3-bromo-2-pyrone will appear in a forthcoming publication dealing with the halogenation of 2-pyrone.